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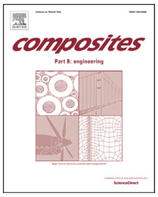

# Thermo-mechanical behaviour and structure of novel bitumen/nanoclay/MDI composites

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ABSTRACT

Novel ternary bituminous composites have been prepared by mixing neat bitumen with an organically modified montmorillonite (Cloisite 20A®) and polymeric MDI (diphenylmethane diisocyanate). Rheological measurements (flow curves and temperature sweeps in oscillatory shear), X-Ray diffraction, Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR) were used to analyse the individual and joint effects of both modifiers. The results obtained show that the addition of 10 wt.% nanoclay provokes a very remarkable enhancement in the bitumen rheological response. The addition of 2 wt.% MDI and subsequent curing at 150 °C, resulting from the chemical interaction between the bitumen/clay composite and MDI, improves the composite properties at low-to-intermediate temperatures but deteriorates them when temperature is further increased.

## 1. Introduction

Based on its solubility in n-alkanes, bitumen components can be separated into two major fractions, maltenes and asphaltenes. Asphaltenes consist of polar aromatic ring systems and highly condensed planar and heteroatom polar functional groups. The increase of this highly viscous fraction leads to binders with low penetration values, higher softening points and greater viscosity. The maltenic fraction can be further sub-divided into saturates, aromatics (naphtene aromatics) and resins (polar aromatics), depending on their solubility and polarity. Saturates contain most of the waxy components of the bitumen, predominantly consisting of straight and branch-chain aliphatic hydrocarbons. Aromatics are present as both polar and non-polar compounds and, together with saturates, constitute part of the oily fraction of bitumen. Resins are very polar molecules and act as solvent for both oils and asphaltenes, which are mutually insoluble [1,2]. Because of the highly complex combination of these components, bitumen properties are strongly dependent on the temperature and its composition, commonly given by the so-called "SARAs" fractions [3].

Bitumen is usually applied to provide waterproofing and protective coating, as well as for building applications, and as a result of its good viscoelastic properties, it is also widely used as a binder in road construction. However, problems related to temperature susceptibility, such as high-temperature rutting and low-temperature cracking, and ageing processes (mainly caused by oxygen diffusion and UV radiation) may change bitumen properties during its service life, leading to its premature failure [4].

In order to improve bitumen performance, chemical modification by means of different additives has increasingly been applied, especially with the use of reactive polymers [6]. In this sense, it has been widely reported that polymeric MDI (a blend of di-phenylmethane di-isocyanate and its higher homologues) and its derived pre-polymers have shown to improve the thermo-rheological behaviour of the resulting bituminous products for both roofing and road applications [12,13]. The modification happens in several stages depending on the presence of water. Thus, in the absence of water, free –NCO groups in the MDI pre-polymer react with polar bitumen compounds containing active hydrogen atoms (mainly –OH, and >NH) yielding new urethane and urea links (reactions R1 and R2, respectively).

$$R^1-NCO+R^2-OH\rightarrow R^1-NH-COO-R^2 \qquad (R1)$$

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$$R^2-NCO+R^1-NH_2\rightarrow R^2-NH-CO-NH-R^1 \tag{R2}$$

$$R^1-NCO+H_2O\rightarrow R^1-NH_2+CO_2\uparrow \tag{R3}$$

However, when water is present in the medium, it can react with $-NCO$ groups, forming carbon dioxide as well as a highly reactive amine according to reaction R3. Next, this amine can further react with the remaining isocyanate groups following the reaction R2. Consequently, all this set of reactions build up larger molecules through the formation of urethane and urea linkages giving rise to the development of more complex structures.

In addition, recently, layered silicates (nanoclays) have also shown to enhance bitumen properties due to their nanoscale characteristics, such as high aspect ratio or surface functional groups [7].

Most nanoclays are found naturally, being environmentally safe, economical, and sustainable. One of the most frequently used layered silicates is montmorillonite (MMT), which is usually modified using quaternary ammonium salts with alkyl chains, rendering the layered silicate organophilic, with enlarged interlayer spacing [8]. Upon adding the nanoclay to the bituminous and/or polymeric matrix, and mixing at high temperature, so that matrix becomes fluid, its molecules can penetrate between the silicate layers of the nanoclay. Depending on the degree of the dispersion of the clay platelets, mixing gives rise to different kinds of structural morphologies: agglomerated silicate platelets (minimum insertion of matrix molecules), intercalated structure, and exfoliated structure, in which silicate layers are no longer close enough to interact with each other [10,38].

Many researches have been conducted on clay/polymer systems, assessing the influence that different variables, such as concentration, polymer structure, type of clay, time or temperature, have on the modification of the system end properties [15,16,18–23, 36,38,40]. Nevertheless, little research has been carried out in clay/bitumen mixtures. In this regard, recently, some authors have studied the influence that clay structure and concentration exert on the rheological and mechanical properties of the nanoclay-modified bitumen [5,8,10,39]. Others have also investigated ternary systems containing polymer, clay and bitumen, assessing the effect that variables such as temperature, procedure of addition, polymer/clay ratio and concentration have on the final blend properties [7,9,41,42]. Results from these works show that nanoclay-modified bitumen are characterized by a noticeable improvement of its thermorheological and mechanical properties over the unmodified bitumen, leading to a synergistic effect in some cases, when combined with polymers. Accordingly, high performance materials for civil engineering applications, such as roofing, waterproofing or thermal insulation, might be produced by the addition of nanoclay and polymer to bitumen.

In this sense, the addition of polymeric MDI to a nanoclay/bitumen binary system, which seems not to have been reported yet in literature, is carried out in this work, with the goal to combine the specific advantages shown by both modifiers when added separately to bitumen. Hence, novel ternary composites of bitumen, Cloisite 20A® and polymeric MDI were obtained. Firstly, in order to determine the individual effects of nanoclay and MDI on the thermo-rheological and structural properties of the resulting bituminous product, binary mixtures were prepared. Secondly, ternary composites were prepared with the purpose of analysing the combined effects, synergistic or otherwise, of these additives on the composite final properties and shedding some light on the interactions between them and the bituminous matrix.

## 2. Experimental

### 2.1. Materials

Bitumen with penetration grade within the range 160/220 was used as the base bitumen for the composite formulation. Bitumen specifications, given by the values of penetration degree (EN 1426:2007), softening temperature (EN 1427:2007) and composition, reported in terms of the “SARAs” fractions, are shown in Table 1.

The following additives were used as modifying agents:

- Cloisite® 20A (“C20A”, hereinafter), which corresponds to an off white, natural montmorillonite modified with N,N-dimethyl dihydrogenated tallow ($C_{14}-C_{18}$) quaternary ammonium chloride. The cation exchange capacity is 92.6 meq/100 g clay and the hydrogenated tallow is composed by a combination of octadecyl (65 wt.%), hexadecyl (30 wt.%) and tetradecyl (5 wt.%) groups. Chemically, in addition to the organic cation present between the platelets, clays naturally contain hydroxyl groups on the edge of the platelets, which are available for further interaction with other groups. Regarding particle specifications, the weight loss on ignition is 38 wt.%, with moisture content lower than 2 wt.%. Dry particle sizes range from values lower than 2 μm (10 vol.%), to lower than 13 μm (90 vol.%), with an average value of 8 μm. The platelets are approximately 1 nm in thickness, leading to aspect ratio values higher than 50, and according to XRD, the interlayer spacing is 2.42 nm.
- Polymeric MDI (4,4′-diphenylmethane diisocyanate). Supplied by T.H. Tecnic (Spain). It consists of an olygomeric mixture of 4,4′-diphenylmethane diisocyanate, 2,4′ and 2,2′ isomers, and condensation products with more than two aromatic rings. A typical polymeric MDI contains approximately 50 wt.% pure MDI, 30 wt.% tri-isocyanate, 10 wt.% tetra-isocyanate, 5 wt.% penta-isocyanate and 5 wt.% higher homologues. The polymeric MDI used is characterized by an $-NCO$ content of 30 wt.% [37].

### 2.2. Modified binders

Depending on the characteristics of the substances to be blended, two different processing devices were used: a low-shear mixer, composed of a 50 mm four-bladed impeller coupled to the blending device “IKA RW20”, allowing maintaining stirring speeds from 800 to 1000 rpm; on the other hand, the high-shear mixer, based on the rotor-stator principle, is an “Ultraturrax™ T25 digital” coupled to the dispersing accessory with a 25 mm diameter stator, and a rotation speed ranging from 16,000 to 18,000 rpm. Both of them were purchased from IKA (Germany). Samples were processed in metal containers (109 mm diameter and 131 mm height) immersed into a bath with circulating oil.

The modification sequence was as follows:

**Table 1**
Penetration, R&B softening temperature and composition (SARAs fractions) values for base bitumen.

| Specifications | Bitumen 160/220 |
|---|---|
| Penetration (1/10 mm) | 162 |
| R&B softening point (°C) | 42.4 |
| Saturates (wt.%) | 6.05 (0.79)[a] |
| Aromatics (wt.%) | 59.88 (1.70)[a] |
| Resins (wt.%) | 19.80 (2.19)[a] |
| Asphaltenes (wt.%) | 14.27 (1.13)[a] |

[a] Values given as mean (standard deviation).